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Using Factor Analysis to Attribute Health Impacts to Particulate Pollution Sources

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Laden et al. (2000) recently reported results of applying factor analysis to data taken in six cities from 1979 to 1988, identifying airborne particle sources potentially affecting daily mortality. These authors sought relationships between source groups and risk measures using source tracer elements, Se (coal combustion), Pb (light-duty motor vehicle sources), and Si (crustal—soil dispersion). Combined data analyses of this kind may overlook the complexity of source contributions, which have common tracer elements. In one of the cities, Boston, for example, the authors found coal combustion was an important source of mortality risk. For the city of Boston, the authors attribute coal combustion largely to distant upwind regional sources. The emphasis on coal combustion is confounded by the presence of major local sources of residual oil combustion, which contribute V, Se, and S (sulfur as sulfate) to the source apportionment. Evaluation of the source identification using single-element tracer analysis indicates that the detailed chemical composition or profile of major local sources needs to be taken into account in these investigations to minimize misclassification of airborne particle sources with potential adverse health effects.

Factor analysis has been applied by a number of investigators to estimate the contribution of different sources of primary emissions that contribute to ambient concentrations of particulate matter (PM) (Hopke, 1991; NARSTO, 2003). Laden et al. (2000) is one of the few such studies that have attempted to link source emissions with health effects. Analyses estimating source contributions to PM depend in part on detailed knowledge of the chemical composition of PM emissions from many sources that may influence ambient PM concentrations, and the capability to differentiate sources with overlapping chemical composition.

With limited or incomplete knowledge of specific source profiles, generic tracer elements are used to identify sources. These have included selenium (Se) for coal combustion, lead (Pb) for mobile sources prior to removal of Pb from gasoline, silicon (Si) or aluminum (Al) for earth's crustal components, and vanadium (V) for residual oil combustion. While these indicator elements are useful adjuncts to source categories, they generally are not unique to a specific source. The attribution of source contributions to health effects then requires accounting for all of the tracer elements in different sources, in combination with the source for which the tracer is identified. Disaggregation by chemical composition is sometimes done by apportioning chemical components of the ambient particles into mathematically "independent" groupings or factors that can be interpreted as source signals (Hopke, 1991; Koutrakis & Spengler, 1987). In analyses of this kind there is a potential for misidentification of contributing sources because of the inherent uncertainty in the source profiles and the methods of factor analysis. Thus, it normally is necessary to supplement factor analysis with other corroborating information, including emissions inventories and wind direction data to interpret precisely the sources of concern.

The objective of this article is to present an argument for using corroborative information to augment and support results

of factor analysis associating pollution sources with measures of human health effects. In our analysis, we assume, as others conventionally do, that the relation between dose and health response is approximately linear, either with or without a threshold (e.g., Calabrese & Baldwin, 2003). A "saturation" level in the dose-response curve is not postulated, for example, one with a significant, positive health association at low ambient PM concentrations, but with a flatter, possibly insignificant association at higher PM levels. Our study depends on support from the following hypotheses:

1. Unique tracer elements, including Se, Pb, and Si are *necessary but not sufficient* for estimating PM source contributions to health effects.
2. Source contributions calculated from factor analysis for specific locations cannot necessarily be aggregated to estimate a multicity effect on daily mortality.
3. Airborne $PM_{2.5}$ from coal combustion, including sulfate, is a weak to negligible indicator of daily mortality from exposure to airborne particles.
4. If a linear dose-response curve applies, toxicological data developed in the laboratory can be used to support or cast doubt on PM epidemiological results.

The first hypothesis is distinct from that used by Laden et al. (2000); for example, they assumed that the Se tracer concentrations was a *necessary and sufficient condition* to identify the association of coal combustion on daily mortality. The second and third hypotheses are also distinct from these authors. In their paper, they adopted implicitly the opposite hypotheses. The fourth hypothesis is concerned with the application of toxicological data to interpret the apparent differences between particles derived from coal and residual oil combustion. Toxicological data were not used in Laden et al. (2000).

METHODS

To illustrate the implications of the hypotheses just listed, we examined the work of Laden et al. (2000) with regard to their interpretation of source attribution and health effects. The Laden et al. (2000) analysis was based on $PM_{2.5}$ (particulate matter nominally less than 2.5 μm aerodynamic diameter) sampling conducted between 1979 and 1988.

Our methods employed a variety of source characterization data and toxicological results in the literature to illustrate how factor analysis can be improved using corroborative data. Specifically, our methods include: (1) researching and then applying ratios of S/Se* in ambient air, and V/Se from sources of $PM_{2.5}$ emissions; (2) calculating amounts of primary sulfate expected from a source (residual oil power plants) at a

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*The assumption is made that the S/Se ratio remains approximately constant during transport of pollutants great distances. That is, deposition removal of the $PM_{2.5}$ components is the approximately the same.

given monitoring site in Boston, based on elemental contents in residual oil fly ash (ROFA) in research literature; (3) deriving an estimate of secondary sulfate in Boston from nearby local residual oil sources, using materials in research literature; and (4) calculating a mass balance for ambient sulfur in Boston, based in large part on (2) and (3). In addition, we cite toxicological literature on the relative potency of coal fly ash (CFA) and ROFA, and a recent lengthy overview of the toxicology of secondary sulfates and nitrates, to buttress the analysis in (1) through (4).

Using all of the points just raised, we then assess the reasonableness of the factor analysis results of Laden et al. (2000) for Steubenville, and especially Boston, and derive a sulfate mass balance for Boston that suggests that much of the sulfate collected at the local monitor in Watertown comes not from distant coal plants, but from large (1700-MW total) residual oil units approximately 8 km to the east. We research wind rose data to show that in Boston, sources to the east of the monitor would impact the monitor with average frequency, despite an apparent downwind location. Using both the toxicology data and the mass balance work, we suggest an alternate interpretation of some of the Laden et al. conclusions with regard to health impacts from different source categories.

Our third hypothesis recognizes, as do other investigations (e.g., CASAC, 1996; NRC, 1998), that an association between PM mass concentrations and increased risk of mortality is oversimplified. To more precisely identify the apparent harmful effects of particles of different origins, these and other studies indicate that both toxicological and epidemiological evidence should be employed. Our investigation elaborates on the Laden et al. (2000) results associating particles of distinctive properties from different sources and daily mortality.

In the following, the results of Laden et al. (2000) are recapitulated, and inconsistencies are noted, especially for the coal combustion tracer (Se) as well as for S in Boston. Explanations for the inconsistencies are proposed that focus on the importance of local sources, and lead to the suggestion that local $PM_{2.5}$ from residual oil combustion is toxicologically more potent than PM from coal combustion.

BACKGROUND

The Laden et al. (2000) results identify three generic sources aggregated for the six cities that are associated with measures of mortality. These include (a) light-duty motor vehicles (3.4% increase in daily mortality per 10 μg/m^3 of $PM_{2.5}$), (b) coal combustion (1.1% increase in daily mortality per 10 μg/m^3 of $PM_{2.5}$), and (c) crustal material (nonstatistically significant decrease in daily mortality per 10 μg/m^3 increase in $PM_{2.5}$). These authors note that in Boston a residual fuel oil factor also was identified that apparently accounted for a 27% increase in daily mortality per 10 μg/m^3 of $PM_{2.5}$. According to Laden et al. (2000), this factor falls short of statistical significance

TABLE 1
Percent increase in daily deaths and 95% CIs for Se (coal tracer) and S (from Laden et al., 2000)[a]

	Boston	St. Louis	Knoxville	Madison	Steubenville	Topeka	Combined
Se factor	2.8%	0.3%	0.8%	0.9%	1.1%	−3.9%	1.1%
	1.2–4.4	−1.1–1.6	−2.7–4.3	−2.5–4.2	−1.2–3.5	−11.2–3.5	0.3–2.0
Sulfur	7.9%	0.8%	1.0%	4.6%	0.5%	−10.3%	3.0%
	3.9–12.1	−2.4–4.2	−6.8–9.4	−3.0–12.7	−6.8–8.3	−23.1–4.6	0.9–5.2

[a]For Se, percent increase is for a 10-μg/m^3 increase in mass concentration from the coal source; for S, percent increase is for an increase from the 5th to the 95th percentile.

(CI = −2.0 to 57.5%).* Standardized scoring coefficients by element and locality were not provided for the residual oil factor, however, precluding comparison with the other source factors.

The sources were identified by single target elements: light-duty vehicle (Pb), coal combustion (Se), crustal (Si), and residual oil combustion (V)—despite the fact that the chemical composition of emissions contains several elements whose presence overlaps one another. All of the identified combustion sources include a substantial amount of sulfur (S), which Laden et al. (2000) assumed from many studies to be sulfate (predominantly ammonium salts). Some sulfuric acid also may be present in air from all the cities. The sampling sites are all near power plants burning coal or residual oil (Spengler & Thurston, 1983).

Inspection of the Laden et al. (2000) results indicates that the risk estimates for daily mortality from the coal combustion source were small and insignificant for the five cities with the highest Se levels (negative for Topeka). Only for Boston, with its air monitor in Watertown, was the coal combustion coefficient significant. Yet the coal combustion tracer concentration (Se) in Boston (0.7 ng/m^3) was considerably lower than for the other cities such as St. Louis (2.2 ng Se/m^3), Knoxville (1.9 ng Se/m^3), and especially Steubenville (5.2 ng Se/m^3). When results from the six cities were combined, a small but positive and statistically significant result was found for the coal combustion risk factor, evidently driven by the calculation for Boston. The Se results are particularly striking in view of the fact that little coal was used locally around Boston at the time of sampling. Nevertheless, Boston is exposed to varying amounts of pollution, much of which is identified with the transport of pollutants from coal combustion in the Mid-Atlantic states and the Midwest.

The coal combustion factor includes a major sulfur (S) component from atmospheric oxidation of emitted SO$_2$ to sulfate.

A pattern for S (assumed to be sulfate) was found: S levels were lower in Boston than in St. Louis, Knoxville, and Steubenville, but higher than in Topeka and Madison. Table 1 restates the Laden et al. (2000) health risk coefficients and confidence intervals for Se and S for each of the six cities. Table 2 gives the measures of ambient PM$_{2.5}$ and selected elements in the six cities (including V, the target tracer for residual oil combustion).

The results are puzzling in terms of the influence of coal combustion products having a significant mortality risk only in Boston. Local or regional coal combustion is a major Se–S source in the other cities. Why the Boston (Se) risk coefficient is between 2.5 and 9 times larger than in the 3 localities with both higher S (sulfate) and far higher Se also needs to be rationalized. For the S factor, the estimated health risk in Boston is even higher—8 to 16 times higher than in the three cities that have higher Se and S levels than Boston. With the possible exception of Boston, the ambient sulfate in the cities is presumed to be mainly "secondary" in nature, formed principally by atmospheric oxidation of SO$_2$ emissions. If the sulfate is responsible for the mortality associations rather than with other substances traced by Se, why are the risk coefficients so much lower, and insignificant, in the three localities with higher sulfate levels? If a constituent associated with coal combustion is responsible, why is the mortality risk factor so high, and significant, only where the Se indicator is lowest?

The use of Se as a tracer element to determine a coal combustion factor seems appropriate in five of the six cities. However, there are ambiguities in the results noted here that need to be evaluated as a central part of the pollution source–daily mortality response model of Laden et al. (2000). Taking into account evidence presented next, the source-risk factor analysis may overstate the amount of PM$_{2.5}$ from coal in ambient Boston air. Instead, we suggest that a nonnegligible portion of the Se and S in the coal combustion source factor comes from local combustion of residual oil in Boston, with its significant use of residual fuel oil.* Furthermore, emissions from residual oil combustion

*Laden et al. (2000) also consider a manganese (Mn) factor for defining residual oil combustion in Madison, WI, and St. Louis, MO. They derive a smaller coefficient using Mn as the source factor (5.6% for Mn, vs. 27.3% using V as the factor for residual oil use). However, there appears to be virtually no residual oil used in Madison based on ambient data (V concentration of 0.1 ng/m^3 compared with 23.2 ng V/m^3 in Boston), and little in St. Louis (2.0 ng V/m^3). Furthermore, there are several industrial facilities, including secondary metal processing, within 7 km of the sampling site in St. Louis (Spengler & Thurston, 1983), which confound the interpretation of the Mn and V factors.

*According to Energy Information Administration (EIA) data in 1980, about 94% of combined residual oil and coal energy used for electricity generation in Massachusetts came from residual oil. In 1985, after partial conversion to coal of two plants outside of Boston, about 67% of the combined energy expended was from residual oil.

TABLE 2
Levels of PM$_{2.5}$ and selected elements in the six cities (from Laden et al., 2000), with standard deviations
in parentheses

	Boston	St. Louis	Knoxville	Madison	Steubenville	Topeka
PM$_{2.5}$ (μg/m^3)	16.5 (9.2)	19.2 (10.1)	21.1 (9.3)	11.3 (7.5)	30.5 (22.4)	12.2 (7.1)
Sulfur (ng/m^3)	1922 (1392)	2350 (1583)	2556 (1491)	1482 (1327)	4248 (3185)	1368 (1169)
Selenium (ng/m^3)	0.7 (0.9)	2.2 (1.9)	1.9 (1.5)	0.9 (0.8)	5.2 (4.2)	0.8 (0.7)
Vanadium (ng/m^3)	23.2 (19.8)	2.0 (4.4)	1.4 (3.3)	0.1 (2.9)	10.5 (20.4)	0.6 (2.8)
Iron (ng/m^3)	62.2 (53.5)	143.7 (132.7)	116.9 (89.1)	44.1 (45.7)	542.2 (738.3)	72.0 (88.2)

constitute a larger portion of the Se, S, and PM$_{2.5}$ fractions than calculated by Laden et al. (2000).

AMBIGUITY IN THE S AND V FACTORS IN BOSTON AND STEUBENVILLE

To illustrate the need to understand all major sources of tracers, including some that may not be present, we will examine data from both Steubenville and Boston.

For Boston, the contribution from coal combustion requires consideration of pollution from distant sources to the west and southwest since little coal is burned locally. The distant sources include regions of the Midwest and the Southeast that can affect not only Boston but also Steubenville and Knoxville. Ambient particle composition data from rural sites in the Ohio River Valley (Tuncel et al., 1987) indicate an S/Se ratio of about 1700, which can be taken as a regional signature dominated by coal combustion emissions upwind of Boston in the 1980s, or local and regionally near Steubenville. Other coal combustion data from the Northeast also show this measure of the S/Se ratio (EPRI, 1994). The reported ratio of S/Se over 2700 in Boston is high (Table 3) relative to characteristic ratios for the upwind region, and compared to the ratio expected if all of the S found in Boston were from coal combustion relatively distant from the city. In contrast, the reported S/Se ratio in Steubenville of 817 is somewhat lower than expected from the knowledge of S/Se in regional coal supplies. Note that Koutrakis and Spengler (1987) identified a "regional" component for secondary sulfate that contained no V but traces of Se in their source factor.

The factor analysis of Koutrakis and Spengler (1987) attributed 99% of the fine particle mass concentration in Steubenville to various sources, while Laden et al. (2000) were able to attribute only 92% for the same location, leaving 8% residual unaccounted for. One possible reason for the larger (99%) attribution in this earlier study follows from the authors'

separation of sulfate from local and secondary sources. The latter represented 63% of sulfate mass concentration, while the former was estimated at 37%.

According to Koutrakis and Spengler (1987), local sulfate in Steubenville appeared to come primarily from coal and oil combustion. They reported that 5 ng V/m^3 came from local coal and oil combustion, and 2 ng V/m^3 from iron and steel production. For two reasons, we believe that it is likely that virtually all of the local sulfate, as well as up to 7 ng V/m^3 and 4.9 ng Se/m^3, came from over 600 acres of coke ovens about 5 km to the south and from various steel manufacturing operations in and around Steubenville itself.

First, we could not find in the Steubenville area any major uses of oil during the sampling period remotely comparable with a 1700-MW residual oil-fired capacity located about 8 km away from the air monitor in the Boston area. Second, data reported by the U.S. Geological Survey (USGS, 1991) for trace elements in coal suggest that raw coals usually have five to nine times as much V as Se. After combustion in boilers, emissions from (coal-fired) power plants with particulate emission control, such as electrostatic precipitators, usually have an Se/V ratio that favors Se by one to two orders of magnitude (EERC, 1996). This results from the high volatility of Se during combustion of coal and from the preferential collection of V in the particulate control devices. Because neither coke ovens nor steel manufacturing operations, under regulations prevailing in the 1970s, had the level of particulate control found in coal-fired power plants, it makes sense that higher proportions of V relative to Se would be emitted from such operations than from coal-fired power plants.

Other than in Boston, Laden et al. (2000) also identified residual oil as a factor only in Steubenville, based on the presence of V. However, Koutrakis and Spengler (1987) noted that a major part of the V found in this city (8 ng V/m^3, of a total of 15 ng V/m^3) was identified as coming from a Ti pigment

TABLE 3
Ratio of S to Se in six cities (calculated from Laden et al., 2000)

	Boston	St. Louis	Knoxville	Madison	Steubenville	Topeka
S/Se ratio	2746	1068	1345	1647	817	1710

plant. Our exploration of the sources in or near Steubenville at the time period in question does not indicate extensive use of residual oil as a fuel or a chemical feedstock (H. Johnson, Ohio Department of Development, personal communication). Instead, the remaining V found in this city is likely to be associated with emissions from steel production, which involves coking, and manipulation of the steel with V as an additive. Contemporary steels, for example, typically contain about 1% V (Anonymous, 1973).

In summary, had Laden et al. (2000) investigated local sources in greater detail, they might have attributed the V factor to local coal and steel making and not to residual oil. This illustrates the need to fully understand the influence of local sources before interpreting results of a factor analysis.

The logical conclusion from these considerations is to look at the risk factor from residual oil combustion more carefully, particularly in Boston. This city is the only one of the six that had significant local residual oil combustion sources. The residual oil factor components are not reported in Laden et al. (2000), but Schwartz et al. (2002) used the Laden et al. data to estimate fuel oil contributions to $PM_{2.5}$ concentrations.

THE BOSTON COAL COMBUSTION SOURCE MAY BE OVERSTATED

The emissions attributed to coal combustion appear to be overstated for Boston, based on figures in Laden et al. (2000) and the paper by Schwartz et al. (2002). Schwartz et al. (2002) report that Boston has a mean ambient particle concentration of 8.3 μg/m^3 from coal sources (Table 1 of Schwartz et al., 2002), stated explicitly to be based on information in Laden et al. (2000). The 8.3 μg/m^3 figure evidently is calculated by taking the coal factor percentage of $PM_{2.5}$ from Laden et al. (2000), who found that 50% of the $PM_{2.5}$ in Boston is from coal combustion, based upon the Se factor (Table 2 of Laden et al., 2000), and multiplying the mean Boston $PM_{2.5}$ concentration of 16.5 μg/m^3 by 50%.

As an initial assessment of the amount of sulfate in Boston ambient air, we applied the S/Se ratio of 1700 (Tuncel et al., 1987), as a regional signature for coal combustion. This signature has also been found in the Northeast (EPRI, 1994). Assuming for the moment that all the Se in Boston in this time frame was from coal generation, we apply the Se measurement for Boston reported by Laden et al. (0.7 ng/m^3 of Se). The product suggests that 1.2 μg/m^3 of S in Boston would come from coal plants (later we show why a nonnegligible amount of Se in Boston actually may come from residual oil generating units). Using the ratio of molecular weights to convert S to SO$_4$, (96 sulfate/32 sulfur), the sulfate in Boston air would be 3.6 μg/m^3. Assuming that all the sulfate is ammonium sulfate,* we again apply the ratio of molecular weights (1.38

ammonium sulfate/sulfate) to calculate a maximum amount of $PM_{2.5}$ from coal emissions in Boston of 4.9 μg/m^3. [Ambient coal fly ash, CFA, is assumed to be small in Boston. Recent observational evidence in the Pittsburgh area, where regional coal based power plants are prevalent, indicate the CFA component averages about 75–100 ng/m^3 in ambient air (W. Aljoe, personal communication). The fly ash concentration arguably would be lower in Boston, where much less coal was burned in the immediate area of the city at the time of sampling.]

The preceding exercise suggests that the sulfate and therefore the $PM_{2.5}$ from coal emissions in the Boston area may be overstated in Laden et al. (2000), and thus indicates the need to more completely explore sources of S in Boston.

To examine further the S mass distribution among sources, partial sulfur and sulfate balances for Boston are compared, using the Laden et al. (2000) results in Table 4 and our alternative in Table 5. In Table 4, a partial accounting of S sources (as S and sulfate) is listed along with total source contributions as identified by Laden et al. (2000) and listed by Schwartz et al. (2002). The part from coal combustion (as sulfate produced by oxidation of SO_2 in the atmosphere—secondary sulfate) is indicated in Table 4. Additional sulfate is estimated to come from combustion of gasoline (the mobile source factor), and (primary) sulfate from the combustion of residual oil. The latter is also derived, as noted in the Table 4. Other sources include primary and secondary sulfate from the local combustion of distillate oil, diesel fuel, and industry.

If the S/Se ratio is adopted as a measure both of the coal and residual oil contribution, a more realistic source apportionment is derived, which allows for other sources not included in the Laden et al. (2000) factors, including a larger source of S from local residual oil combustion. Using the latter method, primary sulfur alone from residual oil combustion is estimated to be approximately the same concentration as the S from coal combustion (Table 5). Qualitatively, this is consistent with, but somewhat smaller than, the 5/7 fraction of Se that can be attributed to residual oil combustion in the Boston area (discussed later).

If an estimate of the secondary sulfate from residual oil is included, as listed in Table 5, the total residual oil contribution to sulfate in $PM_{2.5}$ at Watertown would be larger than the sulfate from coal combustion. Note also in Table 5 that the total sulfate and S estimated without considering "other" sources in the Boston area could be no lower than about 80% of the observed amount at Watertown. In a metropolitan area using significant quantities of diesel fuel in heavy-duty vehicles, as well as distillate and residual oil in commercial and residential applications, this result is not unexpected.

SELENIUM FROM RESIDUAL OIL COMBUSTION

From the preceding discussions, only Boston appears to have a major source associated with residual oil; these large power plants burning residual oil are calculated to be potentially major

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*In fact, some of the secondary sulfate would be lower molecular weight ammonium bisulfate and sulfuric acid. We make the assumption that all of the sulfate would be ammonium sulfate only to calculate a maximum concentration of ambient sulfate, under the assumption of an S/Se ratio of about 1700.

TABLE 4
Partial sulfate balance for Boston (data taken from Laden et al., 2000)

Source class	Average sulfur concentration ($\mu g/m^3$)	Sulfate concentration ($\mu g/m^3$)	Reported total PM$_{2.5}$ mass concentration ($\mu g/m^3$) (Laden et al., 2000; Schwartz et al., 2002)
Measured total	1.92 ± 1.39	5.8 ± 4.2	16.5
Coal combustion[a]	1.7	5.1	8.3
Motor vehicle[b]	0.06	0.18	4.8
Residual oil[c]	0.08–0.09	0.24–0.28	0.5
Other[d]	(?)	(?)	2.9
Total estimated	1.8	5.5–5.6	16.5

[a]Estimate includes *secondary sulfate*, and is based on assumption that coal combustion S is total S reported by Laden et al. (2000) less estimated for mobile and residual oil S from this table.

[b]Calculation assumes the *maximum primary S* in light duty vehicle PM emissions is ∼10% of Pb content (Hidy,1984; Pierson and Brachaczek, 1976). Pb was ∼40% of the vehicle PM (Hidy, 1984); Pierson & Brachaczek (1976) note that this sulfate estimate may be high from their tunnel measurements, influenced by diesel emissions. However, they also note that the primary sulfate is only about 2% of the fuel sulfur burned in combustion.

[c]Estimate for *primary S* based on assumption that 48–56% of PM$_{2.5}$ from oil combustion is sulfate (Hidy, 1984; Costa & Dreher, 1997).

[d]For example, other sources include diesel transportation, industrial and residential heating oil, and secondary sulfate production from local SO$_2$ sources.

sources of particulate sulfate in the Boston area. Spengler and Thurston (1983) describe the location of the Watertown air monitor and its close proximity to oil combustion sources, including several (formerly) Boston Edison plants located roughly 8 km east of the monitoring site. At the time of sampling, a total of over 1700 MW of residual oil fired electricity generation was located at the Mystic plant in Everett, MA, and the New Boston units in Boston itself, each about 8 km east of Watertown.* One of four units of the Mystic plant and neither of the units at the New Boston plant had particulate emission controls (M. Cohen, Massachusetts Department of Environmental Protection, personal communication). Surface wind data from the National Weather Service indicate that the winds blow from the east toward Watertown between 5% and 8% of the time in spring, summer, and fall.† Given the data reported in 16 directional segments for the wind rose, on average, the wind blows from a given direction about 6.25% of the time. This suggests that the monitoring site would be exposed to the plume from these plants according to this "average".

*Between 1979 and 1986, the oil-burning Brayton Point power plant was partially converted to coal fuel (1980/1981). This plant is approximately 60 km south of Watertown. In addition, the Salem Harbor also was partially converted to coal in 1982. This plant is about 25 km north/northeast of Watertown. Both of these plants continued to burn residual oil during the sampling period.

†In the fall, the wind blows from the east about 5% of the time with half of the winds speeds of 3–5.1 m/s, with the rest between 1.5 and 8.2 m/s. For the spring months, east winds blow about 8% of the time with roughly half the wind speeds in the 3–5.1 m/s range and half in the 5.1–8.2 m/s range. During the summer, east winds blow about 7% of the time, with winds about 60% in the range of 3.1–5.1 m/s, and the remainder between 1.5 and 8.2 m/s. In winter, east winds occur about 2.5% of the time.

The plumes would contain significant primary sulfates (including metallic sulfates), small amounts of secondary sulfate from SO$_2$ oxidation downwind, sulfuric acid, and trace elements (such as V and Se) from the combustion process. Even with dilution of the emissions in the plume from entrainment of ambient air, concentrations of pollution from large sources within 8 km would be an important factor in the ambient sampling, relative to more distant sources.

While residual oil is identified with V as a tracer, oil still contains some Se. Using U.S. Environmental Protection Agency (EPA) data, there is approximately 47 times more V than Se in residual oil on average (U.S. EPA, 2003). If all of the V in Boston air derives from residual oil combustion, then the 23.2 ng V/m^3 reported by Laden et al. (2000) would equate to approximately 0.5 ng Se/m^3 in Boston air from residual oil combustion. The remaining 0.2 ng/m^3 would be identified with regional coal combustion emissions. The value of 0.5 ngSe/m^3 from residual oil combustion in Boston is somewhat uncertain since V and Se concentrations are both variable in residual oil combustion emissions. However, the presence of Se in oil, along with the sulfur balance in Table 5, implies that a nonnegligible amount of Se in Boston air derives from residual oil burning. Comparison of the V found in Boston air with that in the other cities excluding widespread use of oil, St. Louis (2.0 ng V/m^3) and Knoxville (1.4 ng V/m^3), also suggests a major contribution from residual oil combustion in Boston.

As noted earlier, we compared the ratio of S to Se from data in Laden et al. (2000) for the six cities (Table 3). The ratio of S to Se is considerably higher in Boston than in the other localities. One reasonable explanation for a higher S to Se ratio here would be that important sources of S in Boston

TABLE 5
Alternative calculation of partial sulfur balance for Boston

Source class	Average sulfur concentration (μg/m^3)	Average sulfate concentration (μg/m^3)	Reported total PM$_{2.5}$ mass concentration (μg/m^3) (Laden et al., 2000; Schwartz et al., 2002)
Measured total	1.92 ± 1.39	5.8 ± 4.2	16.5
Coal combustion[a]	0.6	1.8	8.3
Motor vehicle[b]	0.06	0.18	4.8
Residual oil (primary)[c]	0.6 ± 0.5	1.8 ± 1.5	0.5 (primary plus secondary)
Residual oil (secondary)[d]	0.3 (0.1–0.6)	0.9 (0.3–1.8)	(See comment directly above)
Other[e]	(0.3)	(1)	2.9
Total estimated	1.9	5.7	16.5

[a]Coal combustion estimate is assumed a regional contribution, less the local residual oil component based on footnote c. If all the Se is assumed to be from coal combustion, and the estimate of S is based on the product of reported Se concentration and the S/Se ratio of 1700, estimated S concentration is 1.2 μg/m^3.

[b] The calculation is the same as in Table 4.

[c]Primary S is calculated assuming that sulfate = (% sulfate in fly ash) $\times$ (V in PM$_{2.5}$)/(% V in fly ash).

[d]Secondary S from residual was estimated assuming an average distance of oil sources of 8 km from Watertown, 1% h^{-1} average conversion SO$_2$ to particle S, and total sulfur as SO$_2$ derives from the fuel S to ash ratio less the primary S component. Sulfur in residual oil burned in Boston between 1979 and 1985 from EIA data is about 1%, and ash content of residual is taken as 0.025% (Dixon, personal communication) to about 0.15% based on 1990 EPRI (2003) PISCES data. The value shown here is the "average" of a range between 0.1 and 0.6 μg S/m^3.

[e]Other sources include the combustion of domestic and commercial fuel oils, diesel fuel, and so on. Estimate by difference.

would have lower Se levels than the sources of S elsewhere. Indeed, this would be the case if residual oil supplied some of the S and Se measured by the monitor. Combustion of residual oil results in formation of primary sulfate, including primary V and Ni sulfate, which is emitted directly from the source—as much as 50% of the PM$_{2.5}$ emitted as residual oil fly ash (ROFA) (Hidy, 1984; Costa & Dreher, 1997). So the close proximity of the 1700 MW of power generation using residual oil would result in the monitor showing significant amounts of S from these plants. The high S to Se ratio found in PM$_{2.5}$ from Boston thus is suggestive that an important fraction of the S in Boston is from local sources of residual oil combustion (Table 5).

Evaluation of the Se tracer derived factors in comparison with composition profiles from fuel combustion shows important differences in the interpretation of the ambient PM$_{2.5}$ data sampled in Boston. The lack of differentiation of regional Se–S and local Se–S sources in this city appears to have led to an overestimate of the significance of coal combustion as a major S source in Boston. Had Laden et al. (2000) separated regional sulfate from local sources, as in a similar factor analysis described by Koutrakis and Spengler (1987), perhaps they would have found a far smaller Se factor associated with regional coal combustion emissions. Instead, the residual oil source Laden et al. (2000) identified may have attained "single city" significance for its factor contribution in Boston, as hypothesized considering the large local sources within the metropolitan area.

POTENTIAL HAZARDS OF PM$_{2.5}$ IN BOSTON

Complementing the Se factor, Laden et al. (2000) also reported a separate mortality risk coefficient for S factor. As was the case for Se, the coefficient for S (sulfate) is much larger in Boston than reported for the other cities, and was (statistically) significant only for Boston. Here we note that S from both coal and residual oil sources evidently are commingled, but the results are strikingly similar to those for Se (see Table 1). If sulfate in ambient PM$_{2.5}$ per se were the cause of premature mortality, then three other cities with higher ambient S concentrations should have risk coefficients for S at least as high as for Boston, and perhaps with higher significance than for Boston. However, the opposite is the case, suggesting the possibility that some PM$_{2.5}$ constituent containing sulfate, possibly primary ROFA, may be more harmful than secondary sulfate in the other localities.

A possible rationale for the apparent difference in potency between ROFA and emissions from coal-burning units (sulfate and coal fly ash, CFA) can be found in toxicological studies. Toxicological results are generally insufficient to reliably demonstrate which PM$_{2.5}$ constituents are most likely to cause premature mortality at ambient concentration levels. However, they do represent one indicator for differentiating potency of suspended material in the air. Costa and Dreher (1997), for example, have reported results that may be relevant to this comparison. They found that large doses of ROFA, much larger than expected from the atmosphere, can cause potentially deadly effects in rodents, albeit at very high, instilled laboratory (not

inhaled) doses. The authors postulated that the adverse effects occur because of the transition metals in the ROFA. They compared several of these effects with those of CFA, which contained far lower levels of such metals. While not completely harmless at such high concentration levels, CFA apparently was considerably more benign than the ROFA. Costa and Dreher reported that "[the high levels of metals such as V and Ni] contrasted with the CFA . . . . When compared to oil fly ash samples, CFA with most of its metal tightly bound induced little, if any, injury, and none of its parameters differed from those of saline control" (p. 1056).

The metals were harmful to the animals whether or not they were soluble. However, the authors determined that the damage to the rodents was worse when the metals were soluble; the metals were about 90% soluble when associated with primary acid sulfate formed during residual oil combustion before the emissions exited the stack. Thus, one explanation for residual oil combustion products being more culpable than products of coal combustion lies in the amount of soluble metal content of the primary $PM_{2.5}$ emissions. The Costa and Dreher (1997) animal studies are supported by other high dosage toxicological studies, for example, Lambert et al. (2000) and Carter et al. (1997).

In an in vitro study of $PM_{1.0}$ and $PM_{2.5}$ coal ash particles generated by a pilot combustor, Aust et al. (2002) showed that "soluble extracts of coal fly ash generated reactive oxygen species [ROS] in vitro and that transition metals [believed to be mainly iron] were likely responsible" (p. 1). In culture, with large doses of CFA, the authors found indirect evidence that human epithelial cells formed ROS. A threshold was apparent.

A link between ROS production in cultured cells and premature mortality from iron in ambient air currently appears tenuous at best. The presence of an apparent threshold in the in vitro tests may also be of importance with regard to ambient iron levels. However, we explore next whether it might be possible that iron levels in CFA would be responsible for the health impacts in Boston.

Laden et al. (2000) include information on ambient $PM_{2.5}$ iron concentrations in each of the six cities. $PM_{2.5}$ iron levels paralleled those for Se and for S (Table 2); they were lower in Boston (62.2 ng/m^3) than in Steubenville (542.4 ng/m^3), St. Louis (143.7 ng/m^3), Knoxville (116.9 ng/m^3), and Topeka (72.0 ng/m^3). Only Madison was lower, at 44.1 ng/m^3. Thus, if $PM_{2.5}$ iron (with or without sulfate, which is also low in Boston) in ambient coal fly ash were responsible for premature mortality, it would be logical to see coal factor health risk coefficients at least as large as Boston's, and with greater significance, in localities with higher $PM_{2.5}$ iron levels; instead, we again see the opposite of a dose-response function. This is virtually the same pattern observed for the Se factor, and for S, for example, we see mortality effects said to be associated with coal, only in Boston, the city with the lowest concentrations of the coal factor (Se) or among the lowest concentrations of other elements strongly linked with coal combustion (S) or more weakly linked with coal combustion (Fe).

Laden et al. (2000) take note of the high concentrations of transition metals in ROFA. They comment that "although the residual oil factor was not significant, it had a large (dose-response curve) slope. Residual oil is rich in metals that have been implicated in some of the toxicity studies. More investigations of oil burning seem warranted" (p. 946).

Toxicological evidence also suggests that secondary sulfate and nitrate, at current ambient levels, are unlikely to be harmful. A recent, exhaustive review of the available toxicology literature for secondary inorganic species (Schlesinger & Cassee, 2003) suggests that these groups of $PM_{2.5}$ are likely not to be harmful. They state that "Evaluation of the toxicological database suggests that these particles have little biological potency in normal humans or animals, or in the limited compromised animal models studied at environmentally relevant levels" (p. 197).

The apparent "weaker" potency of secondary sulfate and CFA relative to ROFA derives partly because both the S and the Se factors produced small and statistically insignificant exposure-response risk coefficients in the five cities studied other than Boston (i.e., the ones with higher coal combustion $PM_{2.5}$, but little or no ROFA, in ambient air). This is supported by the cited toxicological evidence. If coal combustion products were responsible in the Laden et al. (2000) study for "significant" mortality effects in Boston, consistency would require that similar results would have been found in the other cities, all of which have higher coal tracer levels than Boston, and three of which also having higher S concentrations.

Finally, it is important to recall that Laden et al. (2000) reported that the risk coefficients for daily mortality from coal combustion sources were not statistically significant for five of the six cities (one was negative). The risk coefficient for coal emissions was much larger, and statistically significant only for Boston. Thus, the reported statistically significant combined result seems to be driven by the results from Boston. Our results indicate that a reanalysis could change the risk coefficients for coal and residual oil in Boston. This could lead to an insignificant risk coefficient for exposure to coal combustion emissions, and a significant one for residual oil, which for Boston was already 27% per 10 μg/m^3 $PM_{2.5}$ (CI: -2% to 57.5%). As seen from the preceding discussion, generalization of source contributions affecting health risk using the combined multi-city analysis tends to miss potentially important city-to-city differentiation.

Could there be some other explanation for the anomalous Laden et al. (2000) results for coal and oil combustion in Boston? In Boston, a large city of population of 500,000+ with known traffic congestion near Watertown and elsewhere, Laden et al. (2000) estimated a motor vehicle contribution to excess daily mortality smaller than those reported from St. Louis (pop. 400,000+), Madison (pop. 190,000+), and Knoxville (pop. 165,000+), while this component was negative for Topeka (pop. 120,000+) and Steubenville (pop. 22,000+). The traffic source factor is significant in St. Louis

and Knoxville, but not in Boston or the other cities. Information on the location of the $PM_{2.5}$ observation sites is not included in their paper. However, we estimate that the Watertown site is about 1.5 km north of the Massachusetts Turnpike, a major interstate highway. A recent study by Zhu et al. (2002) indicates that vehicular emissions such as ultrafines, CO, and black smoke can be between 5 and 10 times higher within 17 m of a freeway than 100 m from the road. A cohort study by Hoek et al. (2002) indicates an apparent elevated health risk from exposure to roadway emissions—for example, a relative risk of cardiopulmonary mortality (age 55+) of 1.95, compared to those not living within 100 m of a freeway or within 50 m of a major urban road. Thus, risk estimation characterized by a single $PM_{2.5}$ observation site may need to adjust for the spatial distribution of the study population combined with roadway emissions. Taking into account traffic density and roadway proximity along with meteorological conditions could show alternatively an overemphasis on both coal and oil contributions relative to the motor vehicle risk factor.

CONCLUSIONS

This study supports the four hypotheses adopted for examination of empirical $PM_{2.5}$ source contributions to risk factors for mortality. Our evaluation of the identification of major sources (1979–1986) contributing to daily morbidity in six cities reported by Laden et al. (2000) has indicated that the coal combustion source is overestimated for Boston. The high risk factor for daily mortality associated with a coal source is high compared with cities that have larger local coal sources present or that are closer to larger regional emissions from coal plants. Spengler and Thurston (1983) have noted that large coal-fired power plants were about 8 km from the air monitors in the Topeka, Madison, and Knoxville surroundings.

Similarly, calculation of primary and secondary sulfate from nearby sources of residual oil emissions also suggests that much of the S observed at Watertown is from these sources.

Examination of the S/Se and Se/V ratios in the light of easily identified large sources of residual oil combustion suggests that this source is important locally for contributing to sulfate and metal concentrations in $PM_{2.5}$ sampled in Boston.

Toxicological evidence suggests that the large risk coefficient attributed to coal combustion in Boston may be identified with $PM_{2.5}$, containing potentially hazardous concentrations of transition metals with acid sulfate from residual oil emissions.

The results of our analysis indicate the need for a revised factor analysis of the data from the Six Cities Study to more precisely account for the influence of $PM_{2.5}$ from residual oil combustion.

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